Phase optimization and microstructure of Ba-Sr-Ni-Fe-O cathode material

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
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By
ADIT KUMARI
ROLL NO: 109CR0628

Under the Guidance of

Dr. Bibhuti B. Nayak

Department of Ceramic Engineering

National Institute of Technology

Rourkela

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NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA

CERTIFICATE

This is to certify that the thesis entitled, "Phase optimization and microstructure of Ba-Sr-Ni-Fe-O cathode material", submitted by Miss. ADITI KUMARI (Roll no. 109CR0628) in partial fulfilment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

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B B Nayak 13/5/13

Prof. Bibhuti B. Nayak
Department Of Ceramic Engineering
National Institute of technology
Rourkela-769008

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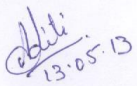

ADITI KUMARI
109CR0628

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ABSTRACT

The Barium Strontium Nickel Ferrite (BSNF) with composition $Ba_{0.5}Sr_{0.5}Ni_xFe_{1-x}O_3$ where x = 0.2, 0.4, 0.6 and 0.8 were synthesized by various routes and with different precursors in order to optimize its pure phase. The various synthesis ways were followed with chloride and nitrates for auto-combustion, microwave assisted synthesis and solid state synthesis with varying various process parameters. Pure phase was obtained via solid state synthesis route with carbonate and oxide as precursors with a sequential firing schedule. The above obtained powder was pressed and sintered at 1000°C. SEM analysis was done to visualize the morphology and particle size. The XRD analysis was done to know the phases present at each synthesis while phase optimisation .The resistivity of the pellet was found in order of mega-ohm, so conductivity measurement could not be done. Apparent porosity and Bulk density measurement was also performed.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Solid oxide fuel cell (SOFC) is an electrochemical device which converts electricity directly from oxidizing a fuel[1],[2],[3],[4]. There are mainly three components of SOFC such as cathode, electrolyte and anode [5],[6].

Perovskites based on alkaline-earth or rare earth containing cobaltite are used for cathode application at lower temperature which involves high electronic and ionic conductivities. Barium strontium cobalt ferrite (BSCF) materials synthesized through various routes are an effective cathode material for SOFCs[7],[8]. If cobalt is replaced by nickel then barium strontium nickel ferrite (BSNF) materials can be used as a cathode material for SOFCs. Latest developments on perovskites showed that these types of material are an attractive option for cathode materials in terms of its high conductivity, excellent oxygen transport and catalytic activity. Also possess a very high rate of oxygen diffusion.

1.2 Literature review

Su et al. [9] synthesized and evaluated Ba0.5Sr0.5Co0.2Fe0.8O3 (BSCF) as cathode in low temperature solid oxide fuel cells using sol gel method. Even at large area (14 cm2) the BSCF can deliver a power density of 358 mW/cm2 and 5 W at 510 ^{o}C.

Toprak et al [10]synthesized BSCF cathode material for solid oxide fuel cells (SOFC) in nanocrystalline form by a novel chemical alloying approach. Co-precipitation method was shown to be a highly feasible route to prepare the desired nanostructured BSCF composition with a high purity. Electrical conductivity measurements show about two times higher conductivity values than best reported BSCF material with the same composition.

Zeljković et al [11] synthesized BSCF powders with perovskite structure from different mixtures of nitrate, oxide and carbonate precursors, irradiated in a microwave oven with 2.45 GHz and various power outputs in oxygen atmosphere. It proved to be efficient and economical. Magnetite, Co (II, III) oxide, Sr carbonate and Ba carbonate can be recommended as the precursors for the microwave assisted synthesis of BSCF.

Kuklja et al [12] studied the Intrinsic Defects, Disordering, and Structural Stability of BSCF Perovskite Solid Solutions. A range of point defects and select relevant solid-solution chemical reactions were explored by means of DFT calculations performed by using large supercells and a variety of ideal and defective BSCF-related crystalline structures. T he new perovskite phases are predicted to nucleate and grow, most likely, on grain boundaries or

surfaces of BSCF, which will significantly impede the efficiency of BSCF-based fuel cell cathodes, separation membranes, and catalysts largely due to the less advantageous oxygen chemistry in those resultant materials.

Han et al [13] fabricated BSCF hollow fibre membranes by a combined phase inversion and sintering technique. The membrane possesses a novel morphology consisting of one dense layer and one porous layer. Oxygen permeation fluxes through the obtained hollow fibre membranes were measured in the temperature range of 650-950 °C using helium sweep gas rates from 50-200 mL min-1. The BSCF hollow fibre membrane showed a stable oxygen permeation flux of 8.60 mL min-1 cm-2 over the investigated period of 120 hours at 900 °C.

Yan et al [14] fabricated and tested BSCF based cathode intermediate temperature solid oxide fuel cell. The evaluated effect of carbon dioxide on the performance of BSCF cathode at temperatures ranging from 450 to 750^{o}C, current density at a constant discharge of voltage value and the electrochemical impedance spectra (EIS) measurements. It showed that as the CO2 content in the cathode side increases and so the operation temperature decreases. It was also shown that as the CO2 content increases, the rate of oxygen electrochemical reduction decreases and the corresponding apparent activation energy increases linearly.

Vazquez et al [15] Synthesized oxyanion-doped barium strontium cobaltferrites and stabilized the cubic perovskite and enhanced in conductivity. For low levels of dopant, a small enhancement in the conductivity was observed. Oxyanion doping improved the stability of the cubic form of BSCF at intermediate temperatures and prevents the transition to a hexagonal cell, and maintains its excellent electrical properties.

1.3 Objective

So, in this project work, we are focusing on phase development of barium strontium nickel ferrite (BSNF) cathode material for SOFC application using different synthesis methods.

CHAPTER 2

EXPERIMENTAL

BSNF sample with different compositions were prepared through different synthesis routes and are described in detail.

Synthesis I

In this synthesis , composition with x= 0.2 , i,e, $Ba_{0.5}Sr_{0.5}Ni_{0.2}Fe_{0.8}O_3$ was formed by auto-Combustion Method. Precursors used were Barium chloride, Strontium chloride, Ferric chloride, Nickel chloride and glycine was used as fuel for combustion. These precursors are added in beaker and then heated and stirred on a hot plate. Solution is heated till gel is formed and once it is formed, stirrer is removed and heating is continued for around 1 to 2 hrs. Then powder is grinded to obtain fine powder. Thus, obtained powder is then calcined at 1000 ^oC with a soaking time of 2 hours.

Synthesis II

In this synthesis, composition with x= 0.8, i,e, $Ba_{0.5}Sr_{0.5}Ni_{0.8}Fe_{0.2}O_3$ was formed by auto-Combustion Method. Precursors used were Barium chloride, Strontium chloride, Ferric chloride, Nickel chloride and glycine was used as fuel for combustion. These precursors are added in beaker and then heated and stirred on a hot plate. Solution is heated till gel is formed and once it is formed, stirrer is removed and heating is continued for around 1 to 2 hrs. Then powder is grinded to obtain fine powder. Thus, obtained powder is then calcined at 1000 ^oC with a soaking time of 2 hours.

Synthesis III

In this synthesis, composition with x= 0.2, i,e, $Ba_{0.5}Sr_{0.5}Ni_{0.2}Fe_{0.8}O_3$ was formed by auto-Combustion Method. Modification from previous synthesis in this was addition of nitric acid in precursors and change in firing schedule. So, here Precursors used were Barium chloride, Strontium chloride, Ferric chloride, Nickel chloride, nitric acid and glycine was used as fuel for combustion. These precursors are added in beaker and then heated and stirred on a hot plate. Solution is heated till gel is formed and once it is formed, stirrer is removed and heating is continued for around 1 to 2 hrs. Then powder is grinded to obtain fine powder. Thus, obtained powder is then calcined at 600^oC for 2 hr , then fine grinding and then 800^oC for 2 hr , then fine grinding then 950^oC for 8 hr , then fine grinding

Synthesis IV

In this synthesis, composition with x= 0.4 , i,e, $Ba_{0.5}Sr_{0.5}Ni_{0.4}Fe_{0.6}O_3$ was formed by auto-Combustion Method. Modification from previous synthesis in this was change in precursors to

nitrates and change in firing schedule. So, here Precursors used were Barium nitrate, Strontium nitrate, Ferric nitrate, Nickel nitrate, citric acid, ammonium nitrate and glycine was used as fuel for combustion. These precursors are added in beaker and then heated and stirred on a hot plate. Solution is heated till gel is formed and once it is formed, stirrer is removed and heating is continued for around 1 to 2 hrs. Then powder is grinded to obtain fine powder. Thus, obtained powder is then calcined at 900^{o}C for 2 hr , then fine grinding then 950^{o}C for 8 hr , then fine grinding.

Synthesis V

In this synthesis, composition with x= 0.4, i,e, $Ba_{0.5}Sr_{0.5}Ni_{0.4}Fe_{0.6}O_3$ was formed by microwave assisted synthesis. Here, precursors used were Barium chloride, Strontium chloride, Ferric chloride and Nickel chloride. In this method, all precursors are added in beaker and then heated and stirred on a hot plate and pH of 13 to 14 is maintained. Solution is heated till gel is formed. Thus precipitated gel is heated in microwave oven for 20 min at interval of 10 minutes each six times. Thus prepared solution was washed again and again till pH dropped to 6 to 7. The precipitate was then dried in oven for 48 hours and then grinds to fine powder. Calcination was then done at 950 ^{o}C for 6 hrs.

Synthesis VI

In this synthesis, composition with x= 0.4 , i,e. , $Ba_{0.5}Sr_{0.5}Ni_{0.4}Fe_{0.6}O_3$ was formed by solid state synthesis.. Modification from previous synthesis in this was change in precursors and change in firing schedule. Here, precursors used were Barium Carbonate, Strontium Carbonate, Nickel oxide and Iron oxide. In this method, estimated amount of barium carbonate is heated at 700^{o}C for 2 hours and strontium carbonate at 1100 ^{o}C for 2 hours to convert into barium oxide and strontium oxide respectively. Thus, formed barium oxide and strontium oxide are mixed properly with estimated amount of nickel oxide and iron oxide. The mix is then fired at 500^{o}C for 2 hr , followed by fine grinding then at 700^{o}C for 4 hr , followed by fine grinding and then 950^{o}C for 8 hr , then grinded.

GENERAL CHARACTERIZATION

Thermal

Thermal analysis were carried out using thermogravimetric and differential scanning calorimetric (TG-DSC) by heating the sample at 10 °C/min in argon in a thermal analyzer (Model STA 4096, NETZSCH , Germany).

X-ray diffraction

Phase analysis was studied using room temperature powder X-ray diffraction with filtered 0.154056 nm Cu Kα radiation. Samples are scanned in a continuous mode from 20° – 80°.

Scanning Electron Microscope

Microstructural features was studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). For preparation of SEM sample, the pellets placed in acetone in an ultra sonication bath (20 kHz, 500 W) for half an hour. These pellets after sonication were used for microscopy. Particle size was obtained from the SEM micrographs.

Apparent porosity and bulk Density

Apparent porosity and Bulk density was measured by using vacuum assisted soaking of pellets in kerosene medium for about 2hr. The dry weight, suspended weight, and soaked weight were taken to calculate bulk density using the following formula.

$$\text{Bulk Density} = D/(W-S) \times \text{density of liquid medium}$$

$$\text{Apparent porosity} = (W-D)/(W-S) \times \text{density of liquid medium}$$

Liquid medium in our case is kerosene with density of 0.80 g/cm^3. Where, D, W, S stands for dry weight, soaked weight and suspended weight respectively of the sample.

CHAPTER 3

RESULTS AND DISCUSSION

Thermal

DSC/TG analysis was performed to understand the mechanism of decompositions and the formation of the final desired BSNF phase. Figure 1 shows DSC-TG curve of BSNF sample prepared through synthesis I. The broad endothermic peak at around 200 °C indicates desorption of water molecule. The exothermic peak at around 950 °C indicates the crystallization temperature of BSNF phase. The phase analysis was done by XRD calcined at 1000 °C.

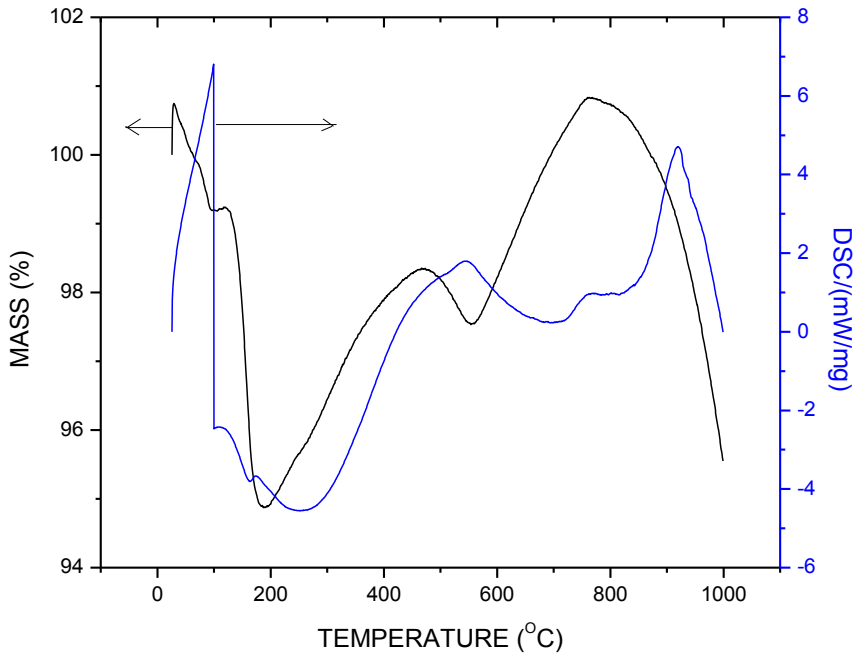

Fig 1: DSC-TG of BSNF sample prepared through synthesis I.

Structure

Figure 2 shows XRD patterns of BSNF sample prepared through synthesis I. As seen from the XRD pattern, the synthesized sample contains impure phase consists of iron oxide, barium iron oxide, barium nickel oxide and strontium iron oxide. Thus, the prepared route is not suitable for preparing BSNF sample.

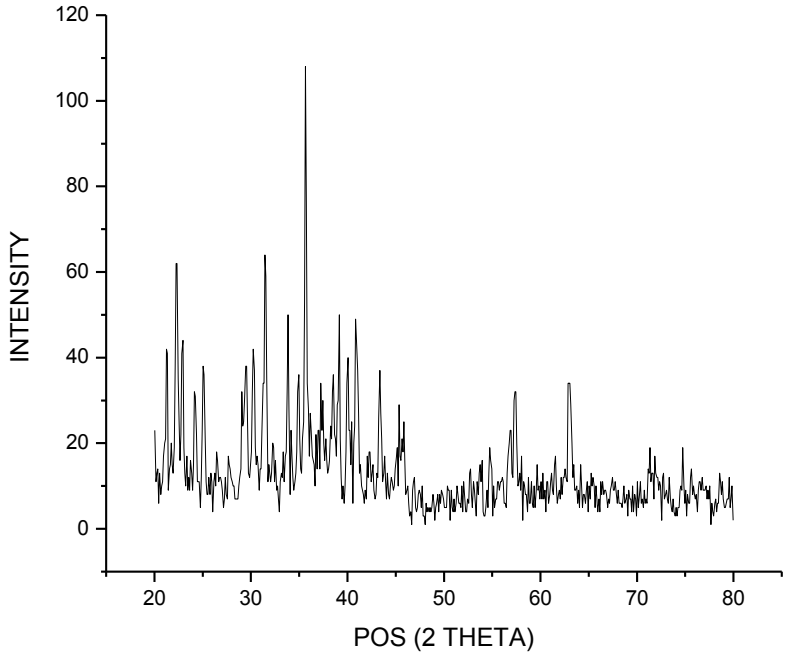

Fig 2: XRD patterns of BSNF sample prepared through synthesis I.

Remark: This method needs further changes in terms of various process parameters in order to optimise purer phase as there are many impurities and unreacted phases. So, synthesis II was carried out for optimization of BSNF phase.

Thermal

DSC/TG analysis was performed for sample synthesized through II route to understand the mechanism of decompositions and the formation of the final desired BSNF phase. Figure 3 shows DSC-TG curve of BSNF sample prepared through synthesis II. The broad endothermic peak at around 150 °C indicates desorption of water molecule. The exothermic peak at around 950 °C indicates the crystallization temperature of BSNF phase. The phase analysis was done by XRD calcined at 1000 °C.

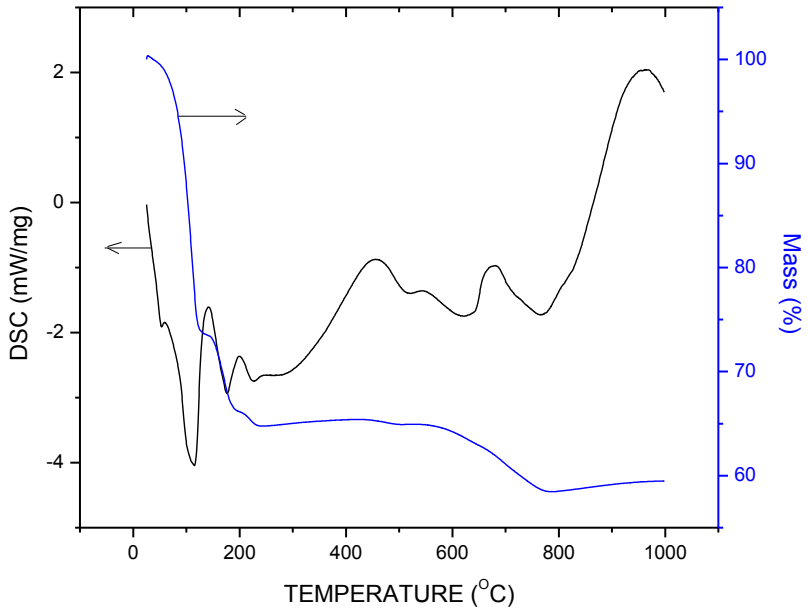

Fig 3: DSC-TG of BSNF sample prepared through synthesis II.

Structure

Figure 4 shows XRD patterns of BSNF sample prepared through synthesis II. As seen from the XRD pattern, the synthesized sample contains impure phase consists of iron oxide, barium iron oxide, barium nickel oxide and strontium iron oxide. Thus, the prepared route is not suitable for preparing BSNF sample.

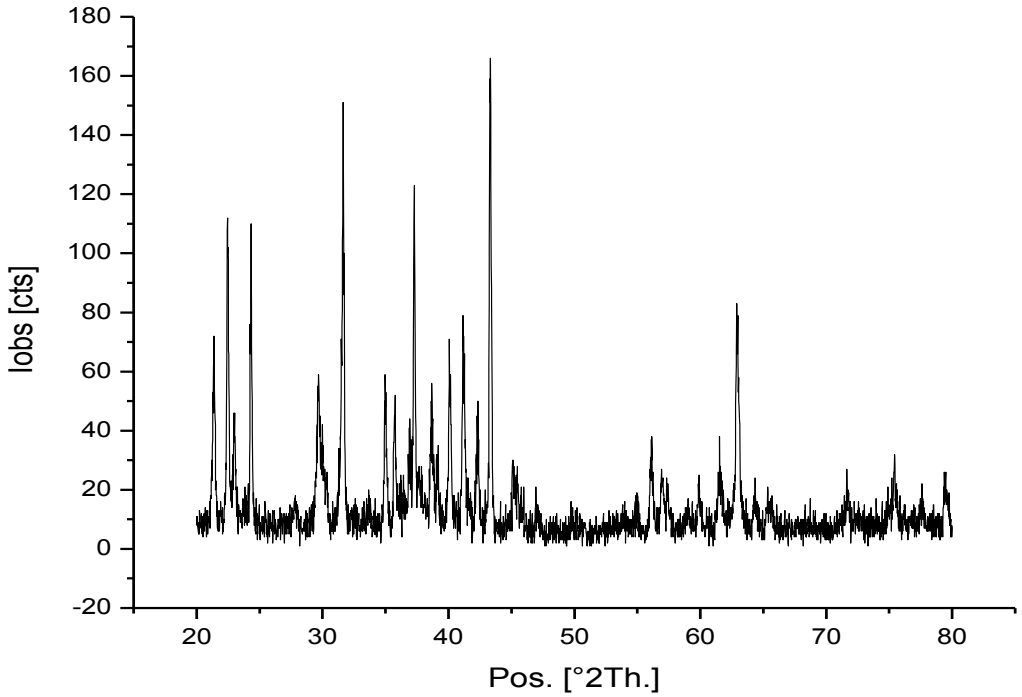

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Fig 4: XRD patterns of BSNF sample prepared through synthesis II.

Remark

This method needs further changes in terms of various process parameters in order to optimise purer phase as there are many impurities and unreacted phases and unidentified peaks. So, synthesis III was carried out for optimization of BSNF phase.

Thermal

DSC/TG analysis was performed for sample synthesized through III route to understand the mechanism of decompositions and the formation of the final desired BSNF phase. Figure 5 shows DSC-TG curve of BSNF sample prepared through synthesis II. The broad endothermic peak at around 100-200 °C indicates desorption of water molecule. The broad exothermic peak at around 950 °C indicates the crystallization temperature of BSNF phase. The phase analysis was done by XRD calcined at 800 °C and 900 °C.

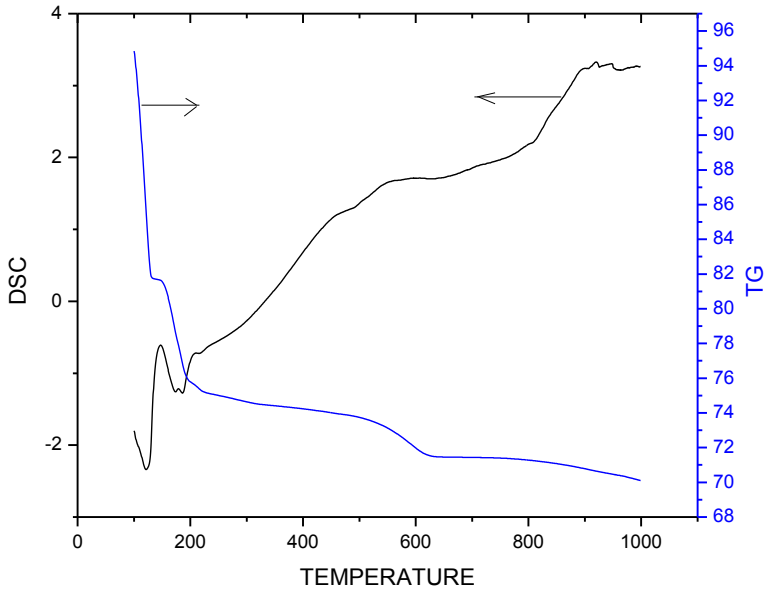


Fig 5: DSC-TG of BSNF sample prepared through synthesis III.

Structure

Figure 6 shows XRD patterns of BSNF sample prepared through synthesis III and calcined at 800 °C and 950 °C. As seen from the XRD pattern, the synthesized sample contains impure phase consists of barium iron oxide, nickel iron oxide, iron oxide, nickel oxide and strontium iron oxide. Thus, the prepared route is not suitable for preparing BSNF sample.

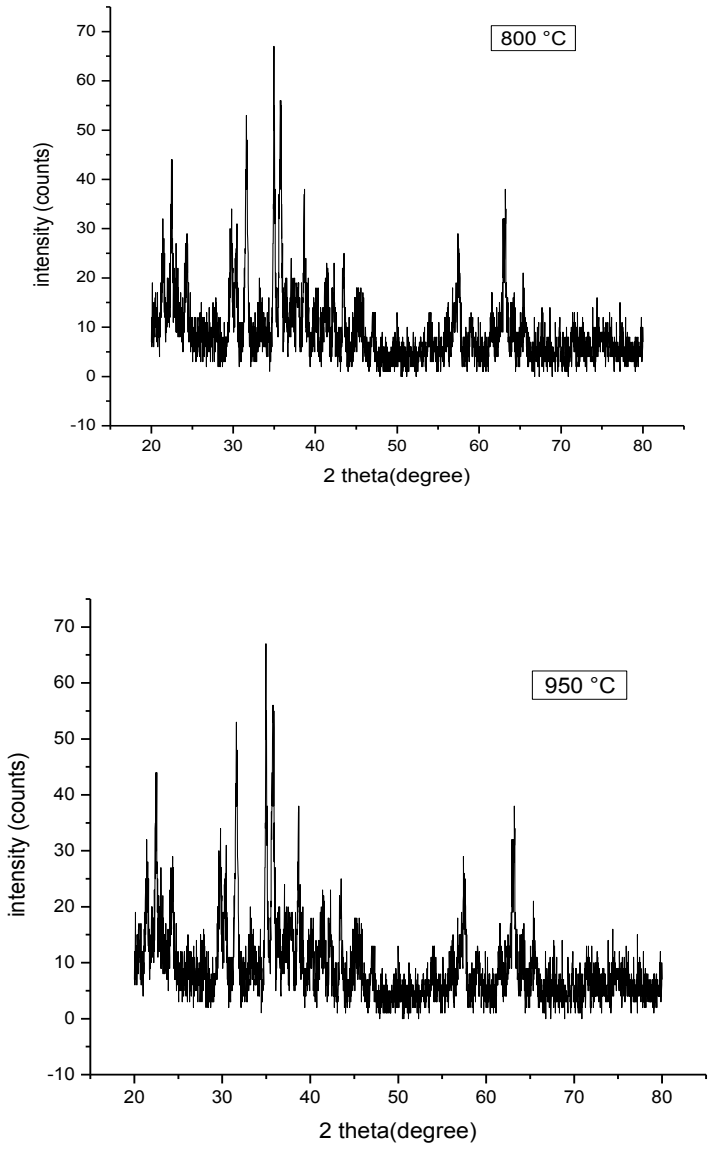


Fig 6: XRD patterns of BSNF sample prepared through synthesis III and calcined at 800 °C and 950 °C.

Upon doing XRD of thus formed powder, though number of unidentified peaks and impurity phases decreased yet there were many such problems and requires further optimisation.

Remark

This method needs further changes in terms of various process parameters in order to optimise purer phase as there are many impurities and unreacted phases and unidentified peaks. So, synthesis IV was carried out for optimization of BSNF phase.

Thermal

DSC/TG analysis was performed for sample synthesized through IV route to understand the mechanism of decompositions and the formation of the final desired BSNF phase. Figure 7 shows DSC-TG curve of BSNF sample prepared through synthesis IV route. The broad endothermic peak at around 100-200 °C indicates desorption of water molecule. The broad exothermic peak at around 950 °C indicates the crystallization temperature of BSNF phase. The phase analysis was done by XRD calcined at 900 °C and 950 °C.

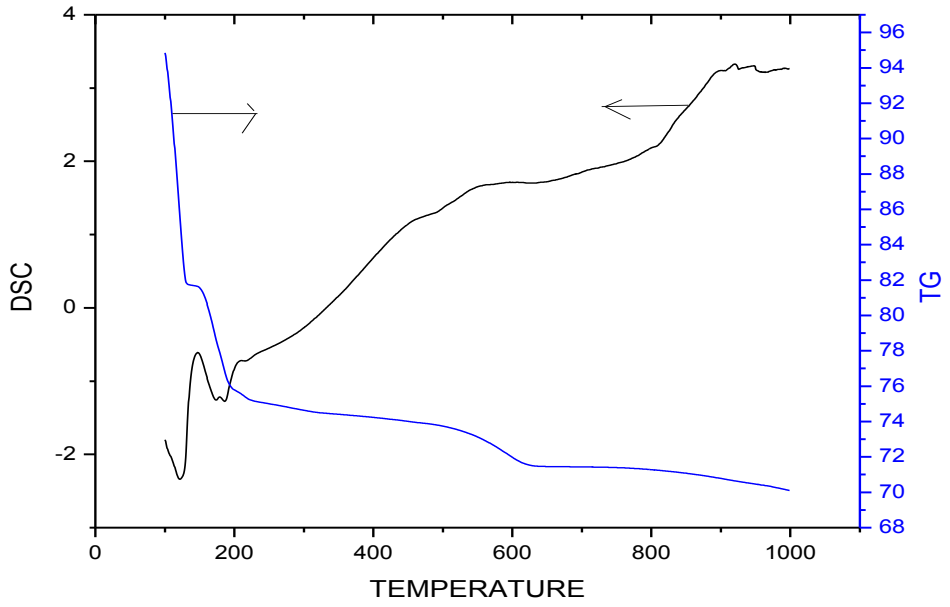


Fig 7: DSC-TG of BSNF sample prepared through synthesis IV.

Structure

Figure 8 shows XRD patterns of BSNF sample prepared through synthesis IV and calcined at 900 °C and 950 °C. As seen from the XRD pattern, the synthesized sample contains impure phase consists of barium iron oxide, strontium nickel oxide, nickel iron oxide, nickel oxide and strontium iron oxide. Thus, the prepared route is not suitable for preparing BSNF sample.

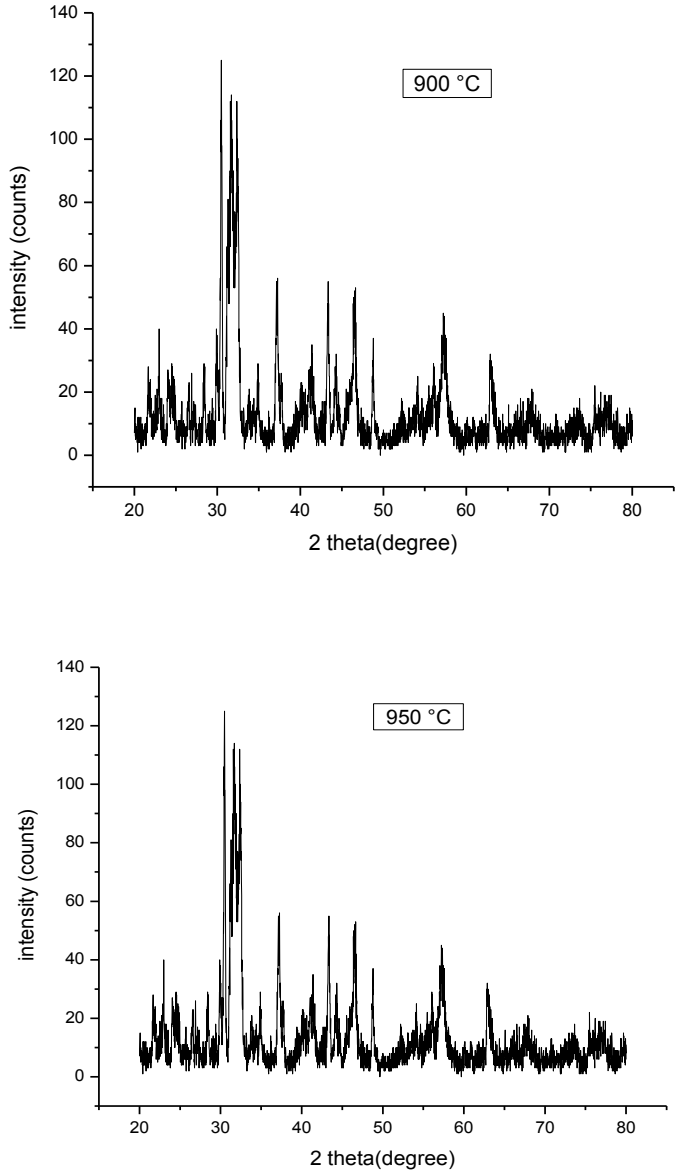


Fig 8: XRD patterns of BSNF sample prepared through synthesis IV and calcined at 800 °C and 950 °C.

Upon doing XRD of thus formed powder, hardly any more improvement was found so yet another trails were to be done to further optimize the pure phase.

Remark:

This method needs further changes in terms of various process parameters in order to optimise purer phase as there are many impurities and unreacted phases and unidentified peaks. So, synthesis V was carried out for optimization of BSNF phase.

Structure

Figure 9 shows XRD patterns of BSNF sample prepared through synthesis V and calcined at 950 °C. As seen from the XRD pattern, the synthesized sample contains impure phase consists of barium iron nickel oxide, barium iron oxide, magnetite and barium strontium iron oxide. Thus, the prepared route is not suitable for preparing BSNF sample.

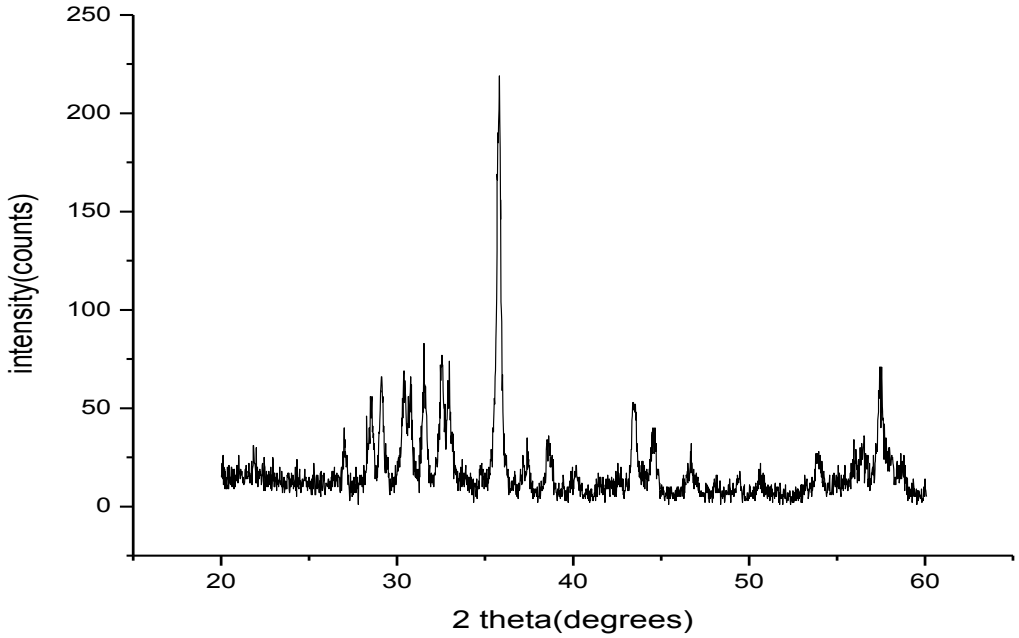


Fig 9: XRD patterns of BSNF sample prepared through synthesis V and calcined at 950 °C.

Remark:

This method needs further changes in terms of various process parameters in order to optimise purer phase as there are many impurities and unreacted phases and unidentified peaks. This method could hardly be optimized to obtain purer phase. So, this method was discarded. So, synthesis VI was carried out for optimization of BSNF phase.

Structure

Figure 10 shows XRD patterns of BSNF sample prepared through synthesis VI and calcined at 950 °C. Peaks were matched with standard literature and most of peaks were found matching with barium strontium cobalt ferrite, only a unidentified peaks of negligible intensity were found. Barium strontium iron oxide was main phase formed with presence of barium nickel oxide. Thus, the prepared route is mostly desirable for preparing BSNF sample.

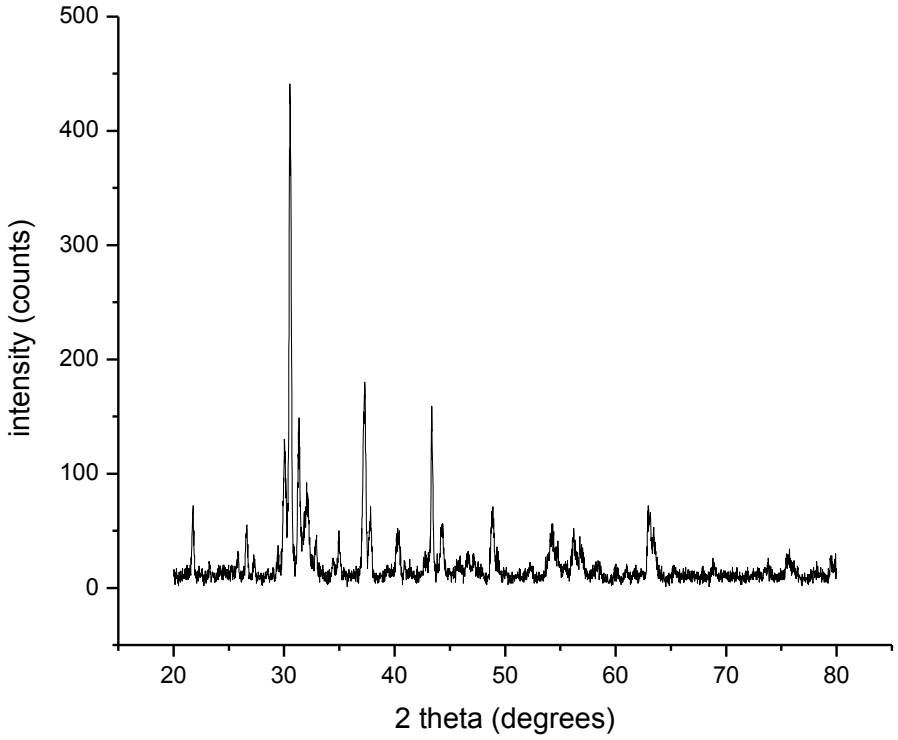


Fig 10: XRD patterns of BSNF sample prepared through synthesis VI and calcined at 950 °C.

Remark

This method is assumed to be able of optimizing the maximum possible pure phase. Though there are some unidentified peaks, they are of very low intensity and all positions of peaks matched with those of literature. This method is opted as method of synthesis further in this project.

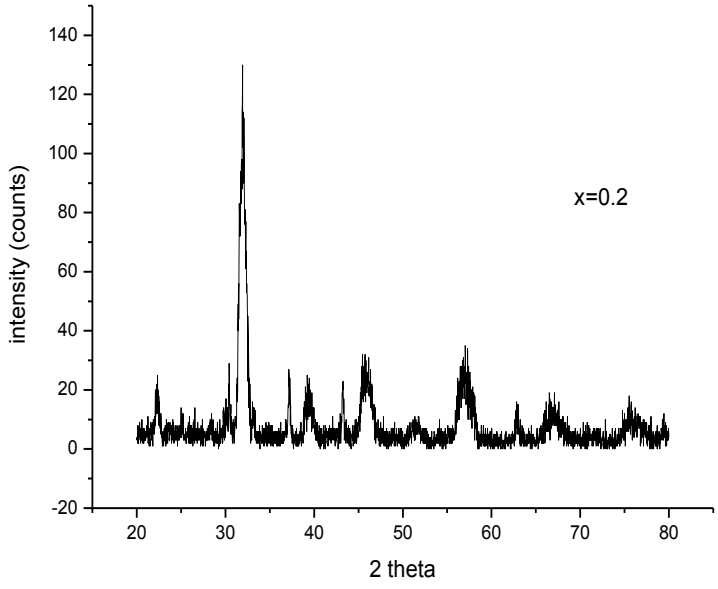
After phase optimization was done, three other compositions were synthesised via solid state route. In total four composition were synthesised, in form of $Ba_{0.5}Sr_{0.5}Ni_xFe_{1-x}O_3$ with x = 0.2, 0.4, 0.6, 0.8. In phase optimization part, composition with x= 0.4 was formed and later other three were also synthesised. Different amount of precursors required for different composition are as follow:

Table 1: Amount of precursors of $Ba_{0.5}Sr_{0.5}Ni_xFe_{1-x}O_3$ with x = 0.2, 0.4, 0.6, 0.8.

Precursors/ composition	Barium Carbonate(gm)	Strontium Carbonate (gm)	Iron Oxide (gm)	Nickel Oxide (gm)
x = 0.2	2.724	2.038	1.762	0.412
x = 0.4	2.723	2.037	1.322	0.821
x = 0.6	2.723	2.037	0.8814	1.237
x = 0.8	2.724	2.037	0.44	1.649

Structure

Figure 11 shows XRD patterns of BSNF sample prepared through synthesis VI and calcined at 950 °C. Peaks were matched with standard literature and most of peaks were found matching with barium strontium cobalt ferrite, only an unidentified peaks of negligible intensity were found.



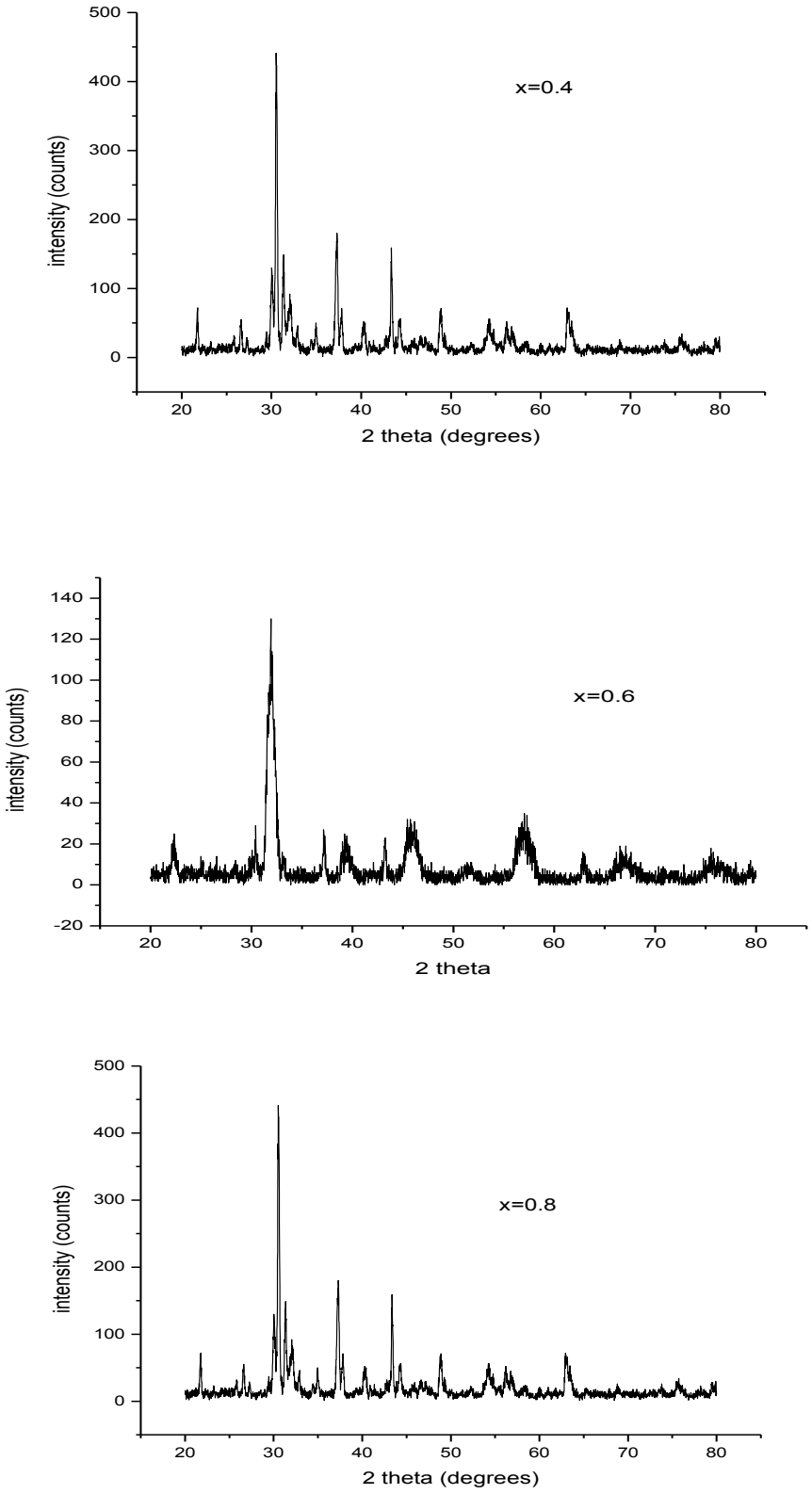


Fig 11: XRD patterns of different compositions of BSNF sample prepared through synthesis VI and calcined at 950 °C.

Microstructure

SEM analysis was conducted to investigate microstructural characteristics of sintered pellet at 1000 ^{o}C. SEM micrographs for smooth and fractured surface were taken at different magnification. Micro sized grains are observed. Microstructure showed a homogeneous composition and microstructural uniformity. Microstructure of fractured piece showed porous structure with micro sized grains. Figure 12 show SEM micrographs of smooth surface of $Ba_{0.5}Sr_{0.5}Ni_{0.4}Fe_{0.6}O_3$ and Figure 13 show SEM micrographs of fracture surface of $Ba_{0.5}Sr_{0.5}Ni_{0.4}Fe_{0.6}O_3$.

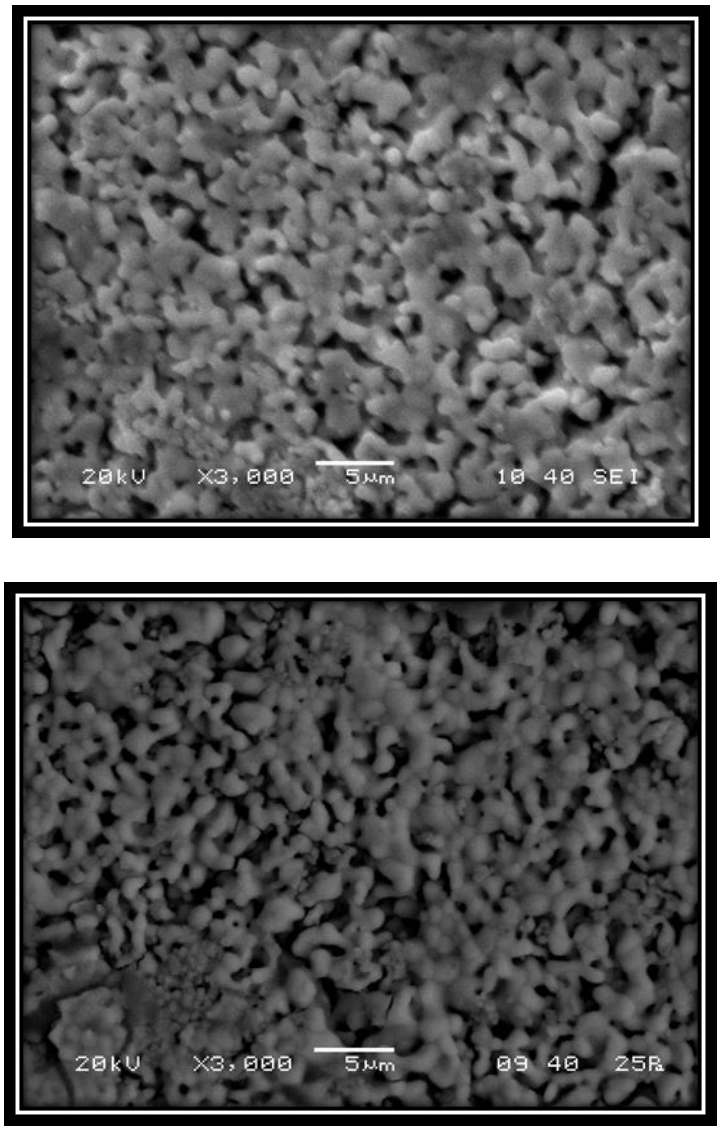


Fig 12: SEM micrographs of smooth surface of composition $Ba_{0.5}Sr_{0.5}Ni_{0.4}Fe_{0.6}O_3$.

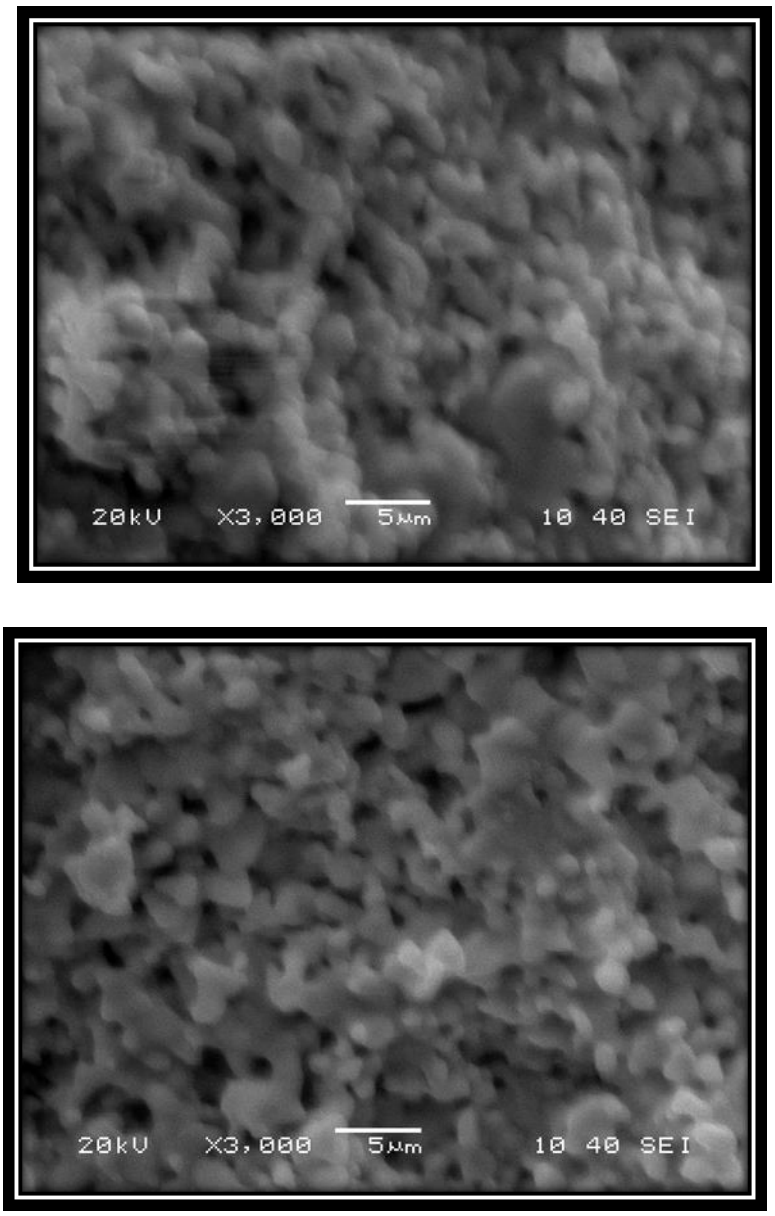


Fig 13: SEM micrographs of fracture surface of composition $Ba_{0.5}Sr_{0.5}Ni_{0.4}Fe_{0.6}O_3$.

Apparent porosity and bulk density

The AP and BD of $Ba_{0.5}Sr_{0.5}Ni_xFe_{1-x}O_3$ were given in Table 2.

Table 2: AP and BD of $Ba_{0.5}Sr_{0.5}Ni_xFe_{1-x}O_3$.

composition	Dry Weight (gm)	Soaked Weight (gm)	Suspended Weight (gm)	Apparent Porosity (%)	Bulk Density
x=0.2	0.701	0.748	0.603	32.4	4.83
x=0.4	0.715	0.764	0.600	29.6	4.36
x=0.6	0.770	0.815	0.658	28.6	4.9
x=0.8	0.786	0.852	0.663	34.6	4.5

FURTHER SUGGESTION

When sintered pellet was measured in multimeter, the resistivity value was found to be in range of mega-ohm, which rendered from doing conductivity measurement. So, further steps are to be taken to reduce resistivity and enhance conductivity. Some possible recommendations for measuring conductivity are:

1. Doping of zinc, to reduce resistivity. This is helpful as demonstrated by literature. According to literature, Zn-doped BSCF demonstrated lower TEC and higher power density than undoped –BSCF.

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2. Incorporation of oxyanions: For low levels of dopant, a small enhancement in the conductivity is observed. It improved the stability of the cubic form of BSCF at intermediate temperatures, helped to prevent the transition to a hexagonal cell, and maintained its excellent electrical properties

CONCLUSIONS

From the experiments it can be concluded that:

- BSNF cannot be prepared from chlorides precursors.
- Pure form of BSNF cannot be obtained through auto-combustion route either with chloride or nitrates as precursors and also via microwave assisted synthesis.
- Pure form of BSNF was obtained by solid state synthesis with carbonate and oxide as precursors.
- XRD analysis confirmed the phase formed with minor impurity.
- SEM analysis confirmed formation of porous microstructure.

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